CLUSTER GEOMETRY OF SUPERCRITICAL Xe
CONFINED IN CARBON MICROPORES.

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INTRODUCTION

Recently various kinds of porous carbon materials have been developed and their properties and structures have been gathering great concerns in science. There are two types of pores of intraparticle pores and interparticle ones[1]. The, carbon nanotube of which pore wall is composed of graphitic sheets has crystalline intraparticle pores[2], when their caps are removed. Activated carbons of the most popular adsorbents are obtained by the activation reaction of carbon materials using H_2O or CO_2. Activated carbon has ill-crystalline intraparticle pores. As activated carbon has excellent adsorptive properties, fine characterization of the pore structure and control of the adsorptive property have been strongly desired. Activated carbon of fiber morphology, so called activated carbon fiber ACF[3], is one of hopeful carbon materials. This ACF has considerably uniform slit-shaped micropores without mesopores, showing excellent adsorption properties. The pore size distribution of ACF is very narrow compared with that of traditional granular activated carbon. Consequently, we can understand more an unresolved problem such as adsorption of supercritical gas using ACF as an microporous carbon.

There are many important supercritical gases such as O_2, N_2, CH_4, NO, and H_2 which are deeply associated with energy, environmental, food, and medical technologies. Further understanding of supercritical gas adsorption is requested to support important technologies. Although vapor adsorption on micropores, which is called micropore filling, is considerably understood, micropore filling of a supercritical gas has not been studied sufficiently irrespective of its importance in micropores[4-7]. We need more fundamental understanding of supercritical gas adsorption. The critical and boiling temperatures of the Xe gas are 289.6K and 165.9K, respectively. The size of a spherical Xe molecule is 0.396nm and the Xe-Xe interaction energy is 217K[8,9]. Accordingly a considerable amount of Xe can be adsorbed in micropores above the critical temperature only by the dispersion interaction. Xe gas has a potential for important applications such as anesthetic and Xe lamp.

In this work, the relationship between micropore filling of supercritical Xe in micropores of ACF at 300 K and cluster size distribution by cluster analysis is described.[10,11]

EXPERIMENTAL

Pitch-based ACFs (P5, P10, and P20) were used. The micropore structures of ACFs were determined by the N_2 adsorption isotherm at 77K using the gravimetric method after the pre-evacuation of ACF samples at 383K. The N_2 adsorption isotherm was analyzed by use of the

in Table 1. The average pore width of these ACFs is in the range of 0.75 to 1.05 nm, corresponding to the model graphite pore.

All adsorption isotherms of supercritical Xe at 300K were onvex in the low pressure range, which can be approximated by the Langmuir equation. In particular, the adsorption isotherm of Xe on P5 having the smallest pores was of

Table 1.   Micropore parameters of pitch-based ACF samples

	Surface Area m^2g^{-1}	Micropore Volume mlg^{-1}	Pore Width nm
P5	900	0.336	0.75
P10	1435	0.614	0.86
P20	2190	1.136	1.05

the representative Langmuir type. The smaller the pore width, the greater the amount of Xe adsorption in the low pressure region. The absolute amount of Xe adsorption was very great even at 60kPa, being larger than 250 mgg^{-1} regardless of the supercritical conditions. The fractional filling values of Xe adsorption at 60 kPa for P5, P10, and P20 were 0.29, 0.14, and 0.09, respectively. Here, the volume occupied by Xe was calculated by use of the bulk liquid density (3.06 gml^{-1} at 159 K).   Then, these ACFs have enough strong molecular field for Xe to be adsorbed even above the critical temperature. In such a case, the DR equation for vapor must be extended to the adsorption of supercritical gas.

Simulated Xe adsorption isotherms

The adsorption isotherms of Xe in the graphite slit pore of $w = 0.90$ to 1.00 nm at 300 K were simulated using the GCMC method.   Both simulated isotherms increase with the Xe pressure and bend upward above 50kPa. In particular, the adsorption isotherm of $w = 0.90$ nm had steeper uptake near 50kPa than that of $w = 1.00$ nm.   The upward bending suggests a strong Xe-Xe interaction, accompanying with the cluster formation.   Although the simulated isotherms did not agree with experimental one, both results indicate the possibility of the cluster formation upon filling of Xe in the micropore. If there is the cluster formation upon filling in the real ACF system, the further adsorption is blocked near the entrance of slightly wedge-shaped micropores due to the cluster formation; the adsorption isotherm should become Langmurian, as observed.

Xe Cluster size distribution and geometrical cluster structures

We analyzed the snapshots obtained from the GCMC simulation at different pressures for $w = 0.90$ nm system.   The cluster analysis evidenced the presence of clusters in the snapshots, giving the cluster size distribution. Before the rising of the isotherm (at 33.7 kPa), 62% of adsorbed Xe molecules are monomers, but we can find 27% of the dimers there; at 50.5 kPa, the percentage of Xe dimers is 30% and even 16% of the trimers are formed. Just after the steep rising at 75.5 kPa, there is the wide distribution of the cluster size; the molecular number in the cluster is in the range up to 12. At 113 kPa the percentage of the monomer drops to 23%, because small Xe clusters merge into greater clusters. Therefore, even above the critical temperature in micropores Xe molecules are associated with each other to form great clusters which can be a precondensed state. This fact supports the idea that predominant adsorption of supercritical gas needs the stable cluster formation between adsorbate molecules.

subtracting pore effect (SPE) method for the α_s-plot with the reference of the standard N_2 adsorption isotherm of nonporous carbon black[3,12]. The high purify Xe gas was adsorbed on ACF samples at 300K after pre-evacuation of ACF samples at 383K and 1mPa for 2 h.   The Xe adsorption isotherm at 300 K was also measured gravimetrically.

GCMC SIMULATION AND CLUSTER ANALYSIS

The established grand canonical Monte Carlo simulation procedure was used.   The random movement of molecules makes new configurations and they are accepted according to Metropolis's sampling scheme[13,14]. The pressure P for a chemical potential was directly calculated from the molecular density using GCMC simulation without the wall potential. The radial distribution function (RDF) was calculated. The intensity of RDF at a distance r was obtained from the average number of molecules which are coordinated at the distance between r and r+Δr (Δr = 0.01nm) for all Xe molecules in 1000 snapshots of the equilibrium state. It was divided by $2\pi r$, because we analyzed only monolayer adsorption region. We used the 12-6 Lennard-Jones potential for the fluid-fluid interaction. The Lennard-Jones parameters of ε_{ff}/k = 276.17K and σ_{ff} = 0.396nm[8,15] were used. The interaction potential of a Xe molecule with a single graphite slab was approximated by Steele's 10-4-3 potential function[16]. The fitted parameters of the Xe-carbon potential well depth and effective diameter (σ_{sf}) were obtained with the use of the Lorentz-Berthelot rules.

We used an established technique of the slit-shaped unit cell in x and y directions[17,19]. The size of the rectangular cell was $l \times l \times w$, where l and w are the unit cell length and slit width, respectively. The rectangular box is replicated two-dimensionally to form an infinite slit shaped micropore. Here, the w is not equal to the physical width of H, which is defined as the distance between opposite carbon atom layers, but w is the empirical slit width which is the pore width from the molecular adsorption experiment. The w is associated with H by eq. 1[20].

$$w = H - (2z_0 - \sigma_{ff}), \quad z_0 = 0.856\sigma_{sf} \tag{1}$$

where z_0 is the distance of closest approach.   In this work, only model graphite model pore of w = 0.90 was calculated.

In the cluster analysis, local molecular configurations of low energy in the equilibrium are presumed to be clusters.   The cluster distribution is obtained using the equilibrium snapshots, when the following function $F(\{n_j\})$ is a minimum. We calculated $F(\{n_j\})$ and determined the cluster distribution using the Metropolis method.

$$F(\{n_i\}) = U(\{n_i\}) - TS(n_i), \quad U(\{n_i\}) = \sum_j U_j, \quad S(\{n_i\}) = k(\ln N! - \sum_j \ln n_j!) \tag{2}$$

Here the number of molecules in the ith cluster is n_i, the total number of molecules N, and the number of ways of allocating N molecules to a given partition $\{n_i\}$. U_j is the cluster formation energy of the cluster j, which consists of n_j molecules; U_j is the sum of each intermolecular potential. $S(\{n_i\})$ is the allocation entropy of partition[21].

RESULTS AND DISCUSSION

Microporosity and adsorption isotherms of supercritical Xe

The adsorption isotherms of N_2 at 77K on three kinds of ACFs were of Type I, indicating the presence of uniform micropores. The N_2 adsorption isotherm was analyzed by the α_s-plot with the subtracting pore effect (SPE) method[12]. Both α_s-plots gave an predominant upward deviation below α_s=0.5 due to the enhanced adsorption. The micropore parameters from these α_s-plots for the N_2 adsorption isotherms were determined by use of the SPE method, as given

The intra-cluster radial distribution RDF at 75.5 kPa was calculated. It had a very short peak at 0.44nm corresponding to the dimer at 33.7kPa for both pores. The peak at 0.44 nm indicates the presence of dimers and trimers of regular triangle shape. Also a week peak at 0.76 nm was observed, suggesting the presence of the complex structure of the regular triangles. Thus, Xe molecules form more and greater clusters having the complex geometrical structure are formed in narrower pores under supercritical conditions.

Acknowledgment

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